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# Single Phase Synthesis, Neutron Diffraction and Dielectric Studies on $0.6PbFe_{0.5}Nb_{0.5}O_3$-$0.4BiFeO_3$ Multiferroic

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**Abstract**. $0.6Pb(Fe_{0.5}Nb_{0.5})O_3$-$0.4BiFeO_3$ (0.6PFN-0.4BFO) multiferroic solid solution was synthesized by single step solid state reaction method. The optimized synthesis parameters for 0.6PFN-0.4BFO multiferroic was calcination at 700 °C /2 hr and sintering at 800 °C /3 hr. Single phase was confirmed though room temperature X-ray Diffraction (XRD) and room temperature Neutron Diffraction (ND). XRD and ND data were well fitted with *monoclinic* structure with *Cm* space group. The magnetic structure was refined using the propagation vector k = (0.5, 0.5, 0.5) and the structure was found to be G-type antiferromagnetic. The dielectric constant and loss tangent of 0.6PFN-0.4BFO shows the frequency and temperature dependent nature. Loss tangent exhibits the thermally dependent relaxation peaks. 0.6PFN-0.4BFO is a potential candidate for above room temperature applications.

**Keywords: Multiferroics, X-Ray Diffraction, Neutron diffraction, Dielectric constant, Dielectric Loss.**

**PACS:** 75.85.+t; 61.05.Cp, 61.05. fm, 78.20.Ci, 77.22.Gm.

## INTRODUCTION

Multiferroics are the materials that exhibits the coexistence of two or more ferroic orders simultaneously in a single material and have many potential applications such as information storage devices, spintronics, sensors and so on [1-3]. The coupling interaction between different order parameters like magnetoelectric, magnetoelastic and piezoelectric effects attracted the scientific community for miniaturization of devices. Till date, the reported number of single phase multiferroic materials is limited due to the simultaneous requirement of $d^0$ and $d^n$ -ness for ferroelectricity and ferromagnetism to occur in a single material [4]. Among them, Pb based multiferroics exhibits high dielectric constant and diffuse ferroelectric phase transition and are used in multilayer capacitor applications. The $PbFe_{0.5}Nb_{0.5}O_3$ (PFN) is a complex perovskite in which $Nb^{+5}$ and $Fe^{+3}$ produce ferroelectricity and ferromagnetism, respectively. It exhibits multiferroic property below 155 K [5] with G type antiferromagnetism. Another well known above room temperature multiferroic is $BiFeO_3$ (BFO). It exhibits multiferroicity below 685 K with *rhombohedral* structure (*R3c* space group) [6].

The synthesis of single phase PFN and BFO is quite difficult by the conventional methods, due to the formation of pyrochlore phases such as $Pb_2Nb_2O_7$, $Pb_2Nb_4O_{13}$ and $Bi_2Fe_4O_9$. In this work, by adopting single step solid state reaction method, we successfully synthesized single phase 0.6PFN-0.4BFO multiferroic at low calcination (700°C /2hr) and sintering (800°C /3hr) temperatures. The detailed structural and electrical properties such as dielectric constant and loss tangent of 0.6PFN-0.4BFO were investigated.

## EXPERMENTAL

The single phase 0.6PFN-0.4BFO solid solution was synthesized through the single step solid state reaction method using stoichiometric amounts of analytic (AR) grade $Pb(NO_3)_2$, $Bi_2O_3$, $Fe_2O_3$ and $Nb_2O_5$ with 1% extra

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$Pb(NO_3)_2$ and $Bi_2O_3$ to compensate the evaporation of lead and bismuth loss during sintering. The detailed synthesis method and optimized conditions were explained elsewhere [7]. Single phase was confirmed by room temperature (RT) XRD (RIGAKU (Ultima IV model) with Cu $K_\alpha$ radiation of wavelength (λ) 1.5406 Å. In order to study the nuclear and magnetic structure of 0.6PFN-0.4BFO in detail, RT ND measurements were measured on FCD (PD-3), a PSD based powder diffractometer at Dhruva Reactor, Trombay, using neutrons of wavelength 1.48 Å. The structural analysis was carried out by Rietveld refinement using Fullprof program. The dielectric constant and loss tangent of 0.6PFN-0.4BFO were investigated as function of frequency (100 Hz–5 MHz) and temperature (133 K - 293 K) by impedance spectroscopy technique.

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## RESULTS AND DISCUSSIONS

The synthesis of Pb and Bi based systems is challenging due to the formation of secondary phases. In order to optimize the synthesis parameters, 0.6PFN-0.4BFO pellets were sintered at different temperatures as well as different duration. Calcination was carried out at 700 °C /2 hr. 0.6PFN-0.4BFO pellets were sintered in a closed alumina crucible with $Pb_{0.5}Bi_{0.5}ZrO_3$ as the packing powder. Figure 1 (a) shows the XRD patterns of 0.6PFN-0.4BFO solid solution sintered at different temperatures i.e. from 800°C to 1000 °C for 1hr duration with an interval of 50 °C. The pyrochlore (%) was calculated from the XRD of each sample using relative integrated intensities of the (222) pyrochlore peak, $I_{pyro}$, and the (111) perovskite peak, $I_{perov}$.

$$\text{pyrochlore (\%)} = \frac{I_{pyro}}{(I_{pyro}+I_{perov})} \times 100 \qquad (1)$$

The pyrochlore percentage evaluated from equation 1was found to be 2.40 %, 2.32 %, 2.88 %, 4.94 % and 6.85 % for 800 °C -1000 °C for 1 hr duration respectively. The sample sintered at 800 °C /1hr exhibits minimum pyrochlore. Next we kept the sintering temperature constant (800 °C) and varied the sintering duration from 1 to 5 hr. Figure 1(b) shows the XRD pattern of 0.6PFN-0.4BFO sample sintered at different duration i.e. 1 to 5 hr. The evaluated pyrochlore percentage was found to be 2.40 %, 2.24 %, 0.0 %, 2.96 % and 3.53 % respectively for 1 to 5 hr duration. Hence, the optimized synthesis parameters are calcination at 700 °C /2 hr and sintering at 800 °C /3 hr. Hence, the low temperature calcination and sintering is observed to be suitable for Pb and Bi based systems in order to avoid the Pb and Bi loss during sintering [8].

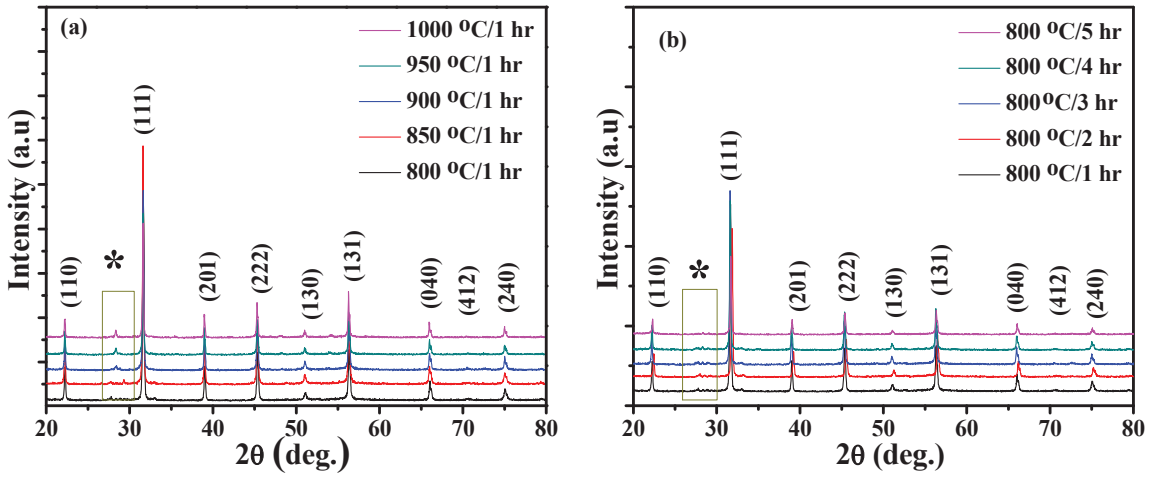


**FIGURE 1:** XRD pattern of 0.6PFN-0.4BFO (a) sintered at different temperature and (b) sintered at different duration.

The structure was studied in detail using RT Neutron diffraction. Rietveld refined RT XRD and ND pattern of 0.6PFN-0.4BFO solid solution are shown in Figure 2 (a and b) and the obtained structural parameters were shown in Table 1. XRD refinement was tried with both *monoclinic* and *rhombohedral* but the best fitting was obtained with

*monoclinic* structure. The nuclear structure of the ND data was also tried with both *monoclinic* as well as *rhombohedral* structure. But all the peaks were well fitted with *monoclinic* structure. After the nuclear structure fitting, one extra peak was observed at 18.03° corresponds to the magnetic ordering and is shown in Figure 2(b) with down side arrow. The magnetic structure was refined using the propagation vector (k) = (0.5, 0.5, 0.5) and it exhibits G type antiferromagnetic structure. The existence of room temperature magnetic ordering in 0.6PFN-0.4BFO can be confirmed through ND. Inset of Figure 2(b) shows the G type antiferromagnetic ordering. In Figure 2(b), N and M stands for nuclear and magnetic Bragg peaks.

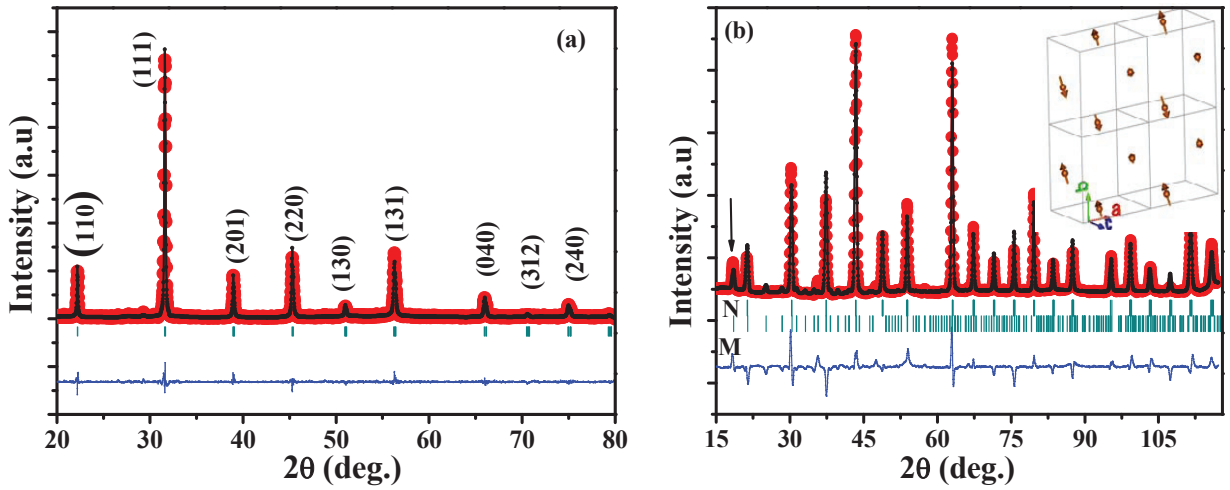


**FIGURE 2:** Rietveld refined (a) XRD (b) ND pattern of 0.6PFN-0.4BFO at RT.

**TABLE 1**. Refined lattice parameters of 0.6PFN-0.4BFO from XRD and ND refinement with *monoclinic* structure.

| 0.6PFN-0.4BFO | a (Å) | b ( Å) | c ( Å) | β(°) |
|---|---|---|---|---|
| XRD | 5.6602(3) | 5.6570(1) | 4.0036(2) | 90.09(1) ° |
| ND | 5.6341(5) | 5.6448(1) | 3.9965(1) | 89.89(1) ° |

Figure 3(a and b) represents the variation of the dielectric constant (ε') and loss tangent (tan δ) as a function of frequency of 0.6PFN-0.4BFO solid solution over a wide range of temperature (173K-293 K). At lower frequencies, the dielectric constant exhibits larger dispersion with maximum value and it becomes almost constant at higher frequencies. Dielectric relaxation phenomena mainly depend on frequency dependent polarisation mechanisms. Different polarisation mechanisms are responsible for the variation of the dielectric constant with respect to frequency. At lower frequency all types of polarisation mechanisms (interfacial, dipolar, ionic and electronic) are in action, but major contribution comes from the interfacial (space-charge) polarisation. At high frequency ($\omega \gg \tau$), the dipoles are unable to follow the applied field and $\varepsilon'$ becomes negligibly small.

The loss tangent increases with increase in frequency. The dielectric loss is high at lower frequencies and decreases as the frequency increases. At lower frequencies, due to Maxwell Wagner interfacial polarisation, large numbers of dipole are trying to orient themselves, giving rise to a large value of the loss. Whereas in the high frequency region, the periodic reversal of the electric field is so fast that there is no excess charge diffusion in the direction of the applied field. This in turn decreases the accumulation of charge, as well the loss tangent value. A peak in the loss tangent occurs at $\omega\tau = 1$, i.e. when the relaxation frequency matches the applied frequency. These relaxation peaks are shifting towards higher frequency with increase in temperature. The loss peaks and their shift with temperature suggest thermally dependent relaxation phenomena in the material [9].

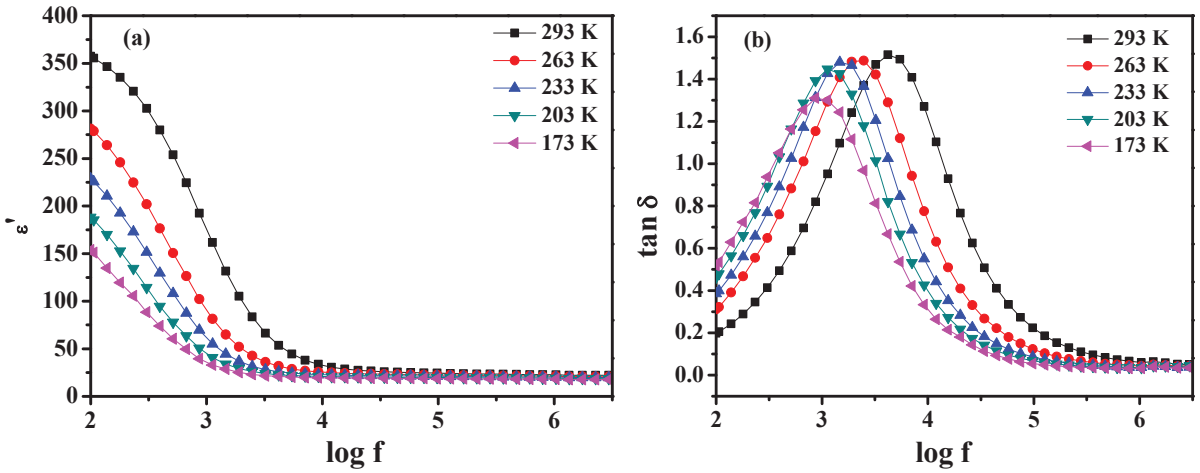


**FIGURE 3**: Dielectric constant (ε') and loss tangent (tan δ) vs. frequency of 0.6PFN-0.4BFO at different temperatures.

In conclusion 0.6PFN-0.4BFO solid solution was synthesized by single step solid state reaction method with lower calcination (700°C/ 2 hr) and sintering (800 °C/ 3 hr) temperature. The XRD peaks well matches with the JCPDS No. 89-8043 and corresponds to the *monoclinic* structure (*Cm* space group). XRD and ND data were well fitted with *monoclinic* structure with *Cm* space group. The RT ND data shows the G type antiferromagnetic ordering. Dielectric constant and loss tangent show the frequency dependent nature with thermally dependent relaxation peaks in loss tangent. 0.6PFN-0.4BFO is a potential candidate for RT multiferroic applications.

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